

# Closure evaluation of size-resolved aerosol pH in the New England coastal atmosphere during summer

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During summer 2002, soluble trace gases, the ionic composition of size-resolved aerosols, and meteorological conditions were measured from the National Oceanic and Atmospheric Administration ship *Ronald H. Brown* in coastal air along the eastern U.S. seaboard. Aerosol acidities were extrapolated from direct pH measurements in minimally diluted extracts and were also inferred from the measured phase partitioning and thermodynamic properties of HCl, HNO<sub>3</sub>, NH<sub>3</sub>, HCOOH, and CH<sub>3</sub>COOH. Median pHs for 0.75- through 25- $\mu$ m geometric mean diameter (GMD) size fractions based on direct measurements (2.6–3.9) were higher than those inferred from HCl partitioning (1.7–3.3). Phase disequilibria caused negative deviations in median pHs inferred from HNO<sub>3</sub> partitioning with aerosol size fractions greater than 2.8- $\mu$ m GMD; pHs inferred for smaller size fractions (median values of 1.9–3.0) were similar to those based on HCl (median values of 1.5–3.0). The pHs inferred from NH<sub>3</sub> partitioning were significantly lower than those estimated by other approaches; causes for this apparent bias are not known. The dominance of gas-phase HCOOH and CH<sub>3</sub>COOH was generally consistent with predicted phase partitioning with acidic aerosols. Typically large diel excursions in most gases implied corresponding variability in aerosol acidity. The pHs inferred from maximum and minimum mixing ratios of gases over each aerosol sampling interval suggested median 12-hour variations of  $\approx$ 0.4–0.7 pH unit. Total acidity ( $H_t = H^+ + \text{undissociated acids}$ ) was greater than  $H^+$  by 1–2 orders of magnitude in all size fractions; most  $H_t$  was in the form of HSO<sub>4</sub><sup>-</sup>.